tic-wave vector is modulated. Unfortunately, the nonuniformity of the fields in the sample<sup>8</sup> makes specification of their magnitude and direction difficult, and our experiments have not yielded the data required for quantitative comparison with theory.

The author is indebted to F. O. R. Miesterfeld for his skilled assistance, and to Dr. R. T. Denton and Dr. B. A. Auld for many helpful discussions. <sup>1</sup>E. G. Spencer and R. C. LeCraw, Phys. Rev. Letters 1, 241 (1958).

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## ANOMALOUS NUCLEAR MAGNETIC RESONANCE LINEWIDTH IN LITHIUM\*

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## and

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The existence of the nuclear magnetic resonance (nmr) linewidth anomaly in lithium and sodium, that the transverse relaxation time,  $T_2$ , is less than the longitudinal relaxation time,  $T_1$ , near the melting point, has been a puzzling question since it was first reported.<sup>1</sup> It is here shown that the anomalous decrease in  $T_2$  observed in lithium is largely due to effects of self-diffusion of lithium in large magnetic field gradients which exist in the small particles used in the nmr experiments. These field gradients exist as a consequence of the bulk susceptibility of the metal.

By using the Carr-Purcell pulse technique<sup>2</sup> it has been possible to minimize the effect of diffusion on the measurement of  $T_2$ . The new measurements of  $T_2$  in lithium are reported here.

The anomaly has existed on the high-temperature side of the diffusion-produced  $T_1$  minimum. In this temperature region, the theory<sup>3</sup> predicts that  $T_2 \approx T_1$ . A value of  $T_2$  that is appreciably less than  $T_1$  implies the existence of some additional spin-spin interaction. If the anomaly is real, then the discontinuity in  $T_2$  upon melting implies a drastic change in this interaction at the melting point. It is important in the study of liquid metals to understand these effects.

Drain<sup>4</sup> has demonstrated that, in a powdered sample, there is an inhomogeneous broadening,  $\Delta H$ , due to the finite susceptibility of the sample. He concludes that a useful approximate expression for this contribution is  $\Delta H \approx 3\chi H_0$ , where  $\chi$ is the magnetic susceptibility and  $H_0$  is the applied external field. In sodium and lithium  $\Delta H \approx 20-40$  milligauss in typical external fields of about  $10^4$  gauss.

In the presence of such an inhomogeneous broadening, the decay constant of a two-pulse (90°-180°) spin-echo envelope<sup>5</sup> should be the true  $T_2$ if the effects of self-diffusion in magnetic field gradients are negligible. Since the distribution of internal fields in powder samples is partly due to irregular particle shape and partly due to random packing of particles, it can be assumed that the internal field should vary by a large fraction of itself over a dimension, R, characteristic of particle size. For 20-micron diameter particles and  $\Delta H \approx 40$  milligauss, the estimated gradient, G, is  $G \approx \Delta H/R \approx 20$  G/cm, which is not small.

The importance of the gradient appears in the expression<sup>2</sup> for the decay of the echo amplitude, M(t),

$$M(t) = M(0) \exp[-t_e (1/T_2 + \frac{1}{12}\gamma^2 G^2 D t_e^2)], \quad (1)$$

where  $\gamma$  is the nuclear gyromagnetic ratio, *D* is the self-diffusion coefficient, and  $t_e$  is the time between the 90° (first) pulse and the echo. In liquid lithium, *D*, estimated from the Stokes-Einstein relation, is ~10<sup>-4</sup> cm<sup>2</sup>/sec,  $\gamma^2 = 1.07$ ×10<sup>8</sup>,  $G \approx 20$  G/cm, and  $t_e$  would be about 80 ×10<sup>-3</sup> sec if  $T_2 = T_1 = 80 \times 10^{-3}$  sec and a typical echo time is used. From these values the diffusion term is  $(\frac{1}{12}\gamma^2G^2Dt_e^{-2})\approx 2\times 10^3$  sec<sup>-1</sup> which is much larger than  $(1/T_2)\approx 13$  sec<sup>-1</sup> for the assumed value of  $T_2$ . [Of course, Eq. (1) was derived for unbounded diffusion in a uniform gradient, G. Also, since there must be a distribution of values of G in a powdered sample, the  $G^2$  used above must be considered to be a mean squared value used for estimations only.]

It has been shown<sup>6</sup> that the Carr-Purcell 90°-180° pulse train can be utilized to minimize the diffusion effects in a sample of small particles. The amplitude of the *n*th echo of the Carr-Purcell train<sup>2</sup> is given by

$$M(t)_{CP} = M(0) \exp\{-t[1/T_2 + (\gamma^2 G^2 D t^2 / 12n^2)]\}.$$
 (2)

The *n*th echo occurs at time  $t = 2n\tau$ , where  $2\tau$  is the 180° pulse spacing. Then

$$M(t=2n\tau)_{\rm CP} = M(0) \exp\{-t[1/T_2 + (\frac{1}{3}\gamma^2 G^2 D\tau^2)]\}.$$
 (3)

The echo decay envelope is exponential, and the measured value of the decay constant is  $(T_2)_m$ , where

$$(T_2)_m^{-1} = [1/T_2 + (\frac{1}{3}\gamma^2 G^2 D\tau^2)].$$
(4)

In the limit of small  $\tau$ ,  $(T_2)_m \rightarrow T_2$ . The  $180^{\circ}$  pulse spacing is small enough if  $(\frac{1}{3}\gamma^2 G^2 D \tau^2) \ll 1/T_2$ . This inequality is met in liquid lithium with  $\tau \ll 3$  milliseconds if the above estimated value of *G* is valid.

Both Carr-Purcell and the two-pulse spin-echo measurements of  $T_2$  were made by Holcomb and Norberg,<sup>1</sup> and they report no difference in the measured values of  $T_2$ . Their values of  $\tau$  may not have satisfied the above inequality.

The gradients produced by the susceptibility should increase with the field so that  $(T_2)_m$  should decrease as the external field is increased. A linear field dependence of  $(T_2)^{-1}$  is reported by Holcomb and Norberg for liquid lithium.

Our measurements of  $T_2$  in lithium by the twopulse spin-echo technique agree with the published numbers of Holcomb and Norberg. The spin-echo envelopes for liquid lithium are not exponential and show diffusion effects for  $t_e \ge 20$ msec.

There is an observed dependence of  $(T_2)_m^{-1}$  on  $\tau^2$  in the Carr-Purcell experiment that is apparent in Fig. 1. The  $\tau$  dependence of  $(T_2)_m^{-1}$  is most pronounced in liquid lithium  $(200^{\circ}\text{C})$  where *D* is large. The lack of linearity of the plot is probably due to the distribution of *G* in the sample and due to the fact that the diffusion occurs in a bounded medium. The average particle size in the mineral-oil dispersion is about 20 microns, and in the liquid state a lithium ion can cross a



FIG. 1. Examples of  $(T_2)m^{-1}$  as a function of  $\tau$  in lithium at 85°C (no detectable diffusion), at 160°C (diffusion in solid lithium), and at 200°C (diffusion in liquid phase). The data designated D.Z. and R.C.W. are from Cornell using off-resonance Carr-Purcell technique. The data designated R.M.C. are from National Bureau of Standards using the on-resonance Meiboom-Gill technique on a different sample.

particle several times in one  $T_2$ . However, even though Eq. (4) cannot be expected to hold exactly, it indicates that the extrapolation of  $(T_2)_m$  to  $\tau$ = 0 should be valid.

At the lowest values of  $\tau$  used,  $\tau = 0.1$  msec,  $(T_2)_m^{-1}$  is about 17 sec<sup>-1</sup> ( $T_2 = 59$  msec) in liquid lithium. The points plotted in Fig. 2 are based upon data at  $\tau = 0.25$  millisecond. An extrapolation to  $\tau = 0$  would raise the plotted points of  $T_2$ in Fig. 2 and make  $T_2$  approach  $T_1$  in liquid lithium. The  $T_1$  measurements are made from 180°-90° pulse combinations and they agree with the results of Holcomb and Norberg. Some typical signals are shown in Fig. 3.

Both the Meiboom-Gill<sup>7</sup> technique and a modified Carr-Purcell train, with the external field about 2 gauss off resonance, were used. These schemes are equally effective in correcting for inaccurate settings of the 180° pulse widths.

Four different samples were used but no large sample effects were observed, especially in the value of  $(T_2)_m$  at short values of  $\tau$ . Two of the samples were dispersions in mineral oil with average particle sizes of ~20 microns and were obtained from different sources. The other two samples were obtained from the dispersions washed in trichloroethylene and exposed briefly to air. The latter two samples were used "dry" and the particles in them remained separated after melting.

In conclusion, the data show that experimental



FIG. 2. Temperature dependence of  $T_1$  and  $T_2$  for <sup>7</sup>Li. The spacing,  $\tau$  (the time between the 90° pulse and the first 180° pulse), in the Carr-Purcell measurement is 250 microseconds.

limitations appear to prevent observing a value of  $T_2$  equal to  $T_1$  in liquid lithium. The Carr-Purcell technique demonstrates the existence of effects of diffusion in large gradients associated with inhomogeneities in sample magnetization. If there is an unknown broadening mechanism in



FIG. 3. Magnetization of <sup>7</sup>Li versus time at temperatures above the melting point (180.5°C). One large division on the time axis equals 9.5 milliseconds. (a) Multiple exposure of two-pulse spin echo at 220°C; (b) echo envelope of Carr-Purcell (Meiboom-Gill) at 205°C with  $\tau = 2.5$  msec for the lower trace and  $\tau = 0.1$  msec for the upper trace. The  $\tau = 0.1$ -msec pulse train is only 45 msec long and is followed by the free-induction decay.

liquid lithium, it must have a strength,  $\Delta \omega$ , of less than 4 sec<sup>-1</sup>.

Also, it is expected that the diffusion effects on measurements of  $T_2$  of <sup>6</sup>Li would show up at lower temperatures since  $(T_2)^{-1}$  for <sup>6</sup>Li is considerably less than  $(T_2)^{-1}$  for <sup>7</sup>Li. Therefore lower values of *D* would upset the inequality relation used above. The onset of the anomaly in <sup>6</sup>Li does indeed occur at lower temperatures.<sup>1</sup> Similarly, a less pronounced deviation in sodium metal would result since  $(T_2)^{-1}$  in sodium is about seven times  $(T_2)^{-1}$  in <sup>7</sup>Li and diffusion is slower in liquid sodium. The above described inhomogeneous broadening mechanism could account for the fielddependent nmr linewidth reported in solid sodium,<sup>8</sup> but it does not account for the increase in linewidth observed above the sodium melting point.<sup>8</sup>

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## EVIDENCE FOR FLUCTUATING AND DIRECT CONTRIBUTIONS TO NUCLEAR REACTION CROSS SECTIONS\*

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We have carried out an analysis of our data on the reactions  ${}^{27}Al(p, \alpha){}^{24}Mg$ , leading to five lowlying states of <sup>24</sup>Mg (spins 0, 2, 3, 4, 0), <sup>59</sup>Co(p,  $(\alpha)^{56}$  Fe,<sup>2</sup> leading to the first three states of <sup>56</sup> Fe (spins 0, 2, 4), and  ${}^{19}F(p, \alpha_0){}^{16}O$ , using the approach of Ericson<sup>3</sup> and Stephen.<sup>4</sup> The data used thus far consist of excitation curves obtained with thin targets (<5 keV) and Van de Graaff resolution (<1 keV), at  $90^{\circ}$  to the proton beam, and bombarding energies of the order of 10 MeV, or excitations in the compound-nuclear systems of about 20 MeV. The principal condition for the applicability of this analysis, namely,  $\Gamma \gg D$ , where  $\Gamma$  is the average width of the compoundnuclear levels (coherence energy), and D is their mean spacing, is certainly satisfied here (see below).

Our main conclusion from this aspect of our  $(p, \alpha)$  data is that there is a very pronounced dependence of the fluctuations on the number of degrees of freedom  $N \sim \frac{1}{2}(2i+1)(2i'+1)(2I+1)$  $\times (2I'+1)$  (where *i*, *i'*, *I*, and *I'* are the spins of projectile, outgoing particle, target, and residual nucleus, respectively), as was predicted.<sup>3,4</sup> Within the accuracy obtainable by this method, we conclude that the theoretical expressions for the probability distributions for the case of no direct-reaction amplitude, i.e., for a purely statistical compound-nucleus régime, account well for the <sup>27</sup>Al and <sup>59</sup>Co data at 90°. The data represent cases for N ranging from 6 to 72, depending upon the various spins involved. Figure 1 shows the probability distributions in the form of histograms for five final states of <sup>24</sup>Mg, with the theoretical curves $^{3,4}$  for the appropriate N values, for zero direct component. Figure 2 shows similar data for three residual states of <sup>56</sup>Fe. For the second excited state, two different energy intervals are shown, with essentially identical results. In all cases the histograms and curves are normalized to area unity. As can be seen, there is no strong indication of any need for direct-reaction admixture here; this is not too surprising in view of the angle of observation. For N = 1 (all spins equal to zero) and pure compound nucleus, the theoretical expression for the probability distribution,  $e^{-x} (x = \sigma/\langle \sigma \rangle)$ , has been confirmed previously.<sup>5</sup> This work represents the first confirmation of the theory for larger N.

A number of facts emerge from such an analysis. In order to have the best possibility of determining the relative proportions of fluctuating (compound-nucleus) and slowly varying (direct-reaction) amplitudes, one must choose cases with small N, i.e., situations with as low spins as possible. Clearly, the case with all zero spins is the most sensitive to degree of mixture. The reason for this is that both large N and large direct-reaction admixtures tend to sharpen the probability distributions about  $\sigma/\langle \sigma \rangle = 1$ , i.e., to lessen the fluctuations about the average. Hence, choosing cases with small N, i.e., with broad distributions as far as N dependence is concerned, any narrowing of the probability curves will reflect the admixture of some direct-reaction amplitude in a sensitive and predictable way, since a closed expression exists for arbitrary N and arbitrary ratio of direct to compound-nuclear amplitude.⁴

In Fig. 3(a) we show the analysis of <sup>19</sup>F(p,  $\alpha_0$ )<sup>16</sup>O,<sup>6</sup> an N = 2 case, at 70° (lab). Clearly, the purely statistical curve no longer suffices, and the theoretical curves for 90% and 95% direct contribution nicely bracket the data. Figure 3(b) shows the situation for <sup>15</sup>N(p,  $\alpha_1$ )<sup>12</sup>C,<sup>7</sup> an N = 10



(b)

FIG. 3. Magnetization of <sup>7</sup>Li versus time at temperatures above the melting point (180.5°C). One large division on the time axis equals 9.5 milliseconds. (a) Multiple exposure of two-pulse spin echo at 220°C; (b) echo envelope of Carr-Purcell (Meiboom-Gill) at 205°C with  $\tau = 2.5$  msec for the lower trace and  $\tau = 0.1$  msec for the upper trace. The  $\tau = 0.1$ -msec pulse train is only 45 msec long and is followed by the free-induction decay.